

This Page Is Inserted by IFW Operations  
and is not a part of the Official Record

## **BEST AVAILABLE IMAGES**

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images may include (but are not limited to):

- BLACK BORDERS
- TEXT CUT OFF AT TOP, BOTTOM OR SIDES
- FADED TEXT
- ILLEGIBLE TEXT
- SKEWED/SLANTED IMAGES
- COLORED PHOTOS
- BLACK OR VERY BLACK AND WHITE DARK PHOTOS
- GRAY SCALE DOCUMENTS

**IMAGES ARE BEST AVAILABLE COPY.**

**As rescanning documents *will not* correct images,  
please do not report the images to the  
Image Problems Mailbox.**

(19)



Europäisches Patentamt

European Patent Office

Office européen des brevets



(11)

EP 1 306 725 A1

(12)

## EUROPEAN PATENT APPLICATION

(43) Date of publication:

02.05.2003 Bulletin 2003/18

(51) Int Cl.7: G03F 1/00, B41C 1/10

(21) Application number: 02023876.2

(22) Date of filing: 24.10.2002

(84) Designated Contracting States:

AT BE BG CH CY CZ DE DK EE ES FI FR GB GR  
IE IT LI LU MC NL PT SE SK TR

Designated Extension States:

AL LT LV MK RO SI

(30) Priority: 24.10.2001 JP 2001326576

26.12.2001 JP 2001394640

11.01.2002 JP 2002005096

18.03.2002 JP 2002074570

18.03.2002 JP 2002074571

12.04.2002 JP 2002111072

12.04.2002 JP 2002111073

14.05.2002 JP 2002138866

06.09.2002 JP 2002261878

02.10.2002 JP 2002290253

(71) Applicant: Toyo Boseki Kabushiki Kaisha  
Osaka-shi, Osaka 530-8230 (JP)

(72) Inventors:

• Wada, Toru,  
c/o Toyo Boseki K.K. Research Center  
Ohtu-shi, Shiga 520-0292 (JP)

- Motoi, Keiichi,  
c/o Toyo Boseki K. K. Research cen  
Ohtu-shi, Shiga 520-0292 (JP)
- Taguchi, Yuji,  
c/o Toyo Boseki K.K. Research Cente  
Ohtu-shi, Shiga 520-0292 (JP)
- Imahashi, Satoshi,  
c/o Toyo Boseki K.K. Research  
Ohtu-shi, Shiga 520-0292 (JP)
- Matsuda, Masaou,  
c/o Toyo Boseki K.K. Head Office  
Osaka-shi, Osaka 530-8230 (JP)
- Takahashi, Kasuo,  
c/o Toyo Boseki K.K. Research  
Ohtu-shi, Shiga 520-0292 (JP)
- Syoki, Koji,  
c/o Toyo Boseki K.K. Research Center  
Ohtu-shi, Shiga 520-0292 (JP)

(74) Representative:

Weber, Thomas, Dr. Dipl.-Chem. et al  
Patentanwälte  
von Kreisler-Selting-Werner,  
Bahnhofsvorplatz 1 (Deichmannhaus)  
50667 Köln (DE)

(54) Photosensitive resin laminate

(57) A photosensitive resin laminate comprising at least a support, a photosensitive resin layer and an IR ablation layer, wherein the IR ablation layer comprises an IR absorbent metal layer which is disposed in contact with the photosensitive resin layer.

on the metal layer can receive an opaque non-transparent to actinic radiation.

(7) The photosensitive resin laminate of the above-mentioned (2), wherein the organic polymer layer laminated on the metal layer contains a UV absorbent.

(8) The photosensitive resin laminate of the above-mentioned (1), wherein the IR ablation layer has an optical density of not less than 2.0.

(9) The photosensitive resin laminate of the above-mentioned (1), which shows a rate of change in the radius of a halftone dot after IR ablation of not more than  $\pm 30\%$  per unit energy ( $J/cm^2$ ).

(10) The photosensitive resin laminate of the above-mentioned (1), which is a photosensitive plate.

(11) The photosensitive resin laminate of the above-mentioned (1), which is a photosensitive flexo plate.

(12) The photosensitive resin laminate of the above-mentioned (11), wherein wrinkles are not caused when a bending radius is not more than 5 cm.

(13) The photosensitive resin laminate of the above-mentioned (11), wherein the IR ablation layer comprises the IR absorbent metal layer and an organic polymer layer laminated on said metal layer, said organic polymer layer being a non-IR-sensitive polymer resin layer and the non-IR-sensitive polymer resin layer comprising a water-soluble polymer and a plasticizer.

(14) The photosensitive resin laminate of the above-mentioned (1), wherein the photosensitive resin laminate is a photosensitive letter press plate.

(15) The photosensitive resin laminate of the above-mentioned (14), wherein the photosensitive resin layer comprises a composition containing a polymer binder, an ethylenically unsaturated compound and a photoinitiator, the photosensitive resin laminate shows a rate of warp of within  $\pm 2\%$  before exposure to actinic radiation, and a change in the warp after exposure to actinic radiation is not more than 15%.

(16) The photosensitive resin laminate of the above-mentioned (14), wherein the photosensitive resin layer has a residual solvent content of 3 - 10%.

(17) A photosensitive resin laminate comprising at least a support, a photosensitive resin layer and an IR ablation layer, wherein the IR ablation layer comprises an IR absorbent metal layer and a UV absorbent organic polymer layer on at least one surface of the metal layer.

## BRIEF DESCRIPTION OF THE DRAWINGS

### [0008]

Fig. 1 is a schematic cross section of a first embodiment of the photosensitive resin laminate of the present invention

Fig. 2 is a schematic cross section of a second embodiment of the photosensitive resin laminate of the present invention.

Fig. 3 is a schematic cross section of a third embodiment of the photosensitive resin laminate of the present invention.

Fig. 4 is an explanatory schematic view of a rate of warp measurement sample.

Fig. 5 is an explanatory schematic view of a rate of warp measurement sample.

## DETAILED DESCRIPTION OF THE INVENTION

[0009] In the following, the present invention is explained in detail.

[0010] The photosensitive resin laminate of the present invention comprises at least a support, a photosensitive resin layer and an IR ablation layer, wherein the IR ablation layer comprises an IR absorbent metal layer and the metal layer is disposed in contact with the photosensitive resin layer.

[0011] Figs. 1, 2 and 3 show examples of the laminate structure of the photosensitive resin laminate of the present invention. Fig. 1 shows a constitution wherein a support 1, a photosensitive resin layer 2, an IR absorbent metal layer 3 and a cover film 5 are successively laminated, and Fig. 2 shows a constitution wherein a support 1, a photosensitive resin layer 2, an IR absorbent metal layer 3, an organic polymer layer 4 and a cover film 5 are successively laminated. Fig. 3 shows a constitution wherein the organic polymer layer 4 in Fig. 2 is a non-IR sensitive polymer resin layer 6, or a constitution wherein a support 1, a photosensitive resin layer 2, an IR absorbent metal layer 3, a non-IR sensitive polymer resin layer 6 and a cover film 5 are successively laminated.

[0012] In the example of Figs. 1, 2 and 3, an IR ablation layer 10 is made only of the IR absorbent metal layer 3, and in the example of Fig. 2, an IR ablation layer 10 is made only of two layers of the IR absorbent metal layer 3 and the organic polymer layer 4 formed thereon.

[0013] In the photosensitive resin laminate of the present invention, as shown in the examples of the above-mentioned Fig. 1, Fig. 2 and Fig. 3, the IR ablation layer 10 includes the IR absorbent metal layer 3. As a result, the IR ablation

a main chain by secondary reaction with a compound reactive with hydroxyl group of polyvinyl alcohol (e.g., a compound having carboxyl group, double bond, aromatic ring and the like) or saponification of a copolymer of vinyl acetate and a different vinyl monomer.

[0026] The organic polymer layer of the present invention has a thickness of 0.01 - 200  $\mu\text{m}$ , preferably 0.1 - 100  $\mu\text{m}$ , particularly preferably 0.1 - 50  $\mu\text{m}$ . When the thickness exceeds 200  $\mu\text{m}$ , it may not be easily set on a drum for IR-ablation, or the relief obtained by main exposure and development may show lower resolution, which is not preferable. The organic polymer layer 4 may contain a compound that absorbs ultraviolet rays, such as UV absorbent, metal and the like for the prevention of fogging phenomenon during main exposure.

[0027] Preferably, the above-mentioned organic polymer layer laminated on the metal layer is a non-IR-sensitive polymer resin layer.

[0028] Preferably, the above-mentioned organic polymer layer laminated on the metal layer contains a UV absorbent.

[0029] As a method for adding a UV absorbent to the organic polymer layer, there is a method comprising adding a UV absorbing substance to the organic polymer layer, a method comprising copolymerization of a reactive UV absorbing substance with a monomer to give a polymer layer and the like.

[0030] Examples of the UV absorbing substance include general UV absorbents, such as benzophenone compound, benzotriazole compound, salicylate compound, indole compound and the like. Examples of the benzophenone compound include 2,4-dihydroxybenzophenone, 2-hydroxy-4-methoxybenzophenone, 2-hydroxy-4-octoxybenzophenone, 2-hydroxy-4-benzyloxybenzophenone, 2-hydroxy-4-dodecyloxybenzophenone, 2,2'-dihydroxy-4-methoxybenzophenone, 2,2'-hydroxy-4,4'-dimethoxybenzophenone, 2-hydroxy-4-methoxy-5-sulfobenzophenone and the like. Examples of the benzotriazole compound include 2-(2'-hydroxy-5'-methylphenyl)benzotriazole, 2-(2'-hydroxy-5'-tert-butylphenyl)benzotriazole, 2-(2'-hydroxy-3',5'-ditert-butylphenyl)benzotriazole, 2-(2'-hydroxy-tert-butyl-5'-methylphenyl)-5-chlorobenzotriazole, 2-(2'-hydroxy-3',5'-ditert-butylphenyl)-5-chlorobenzotriazole, 2-(2'-hydroxy-3',5'-ditert-amylphenyl)benzotriazole, 2-(2'-hydroxy-3'-(3",4",5",6"-tetrahydronaphthalimidermethyl)-5'-methylphenyl)benzotriazole and the like. Examples of the salicylate compound include phenylsalicylate, p-tert-butylphenylsalicylate, p-octylphenylsalicylate and the like.

In addition, a compound having a naphthalene skeleton such as 2-hydroxy-3-naphthoic acid propylene glycol ester and the like, a compound having an anthracene skeleton such as 9-anthracenemethanol and the like, a compound having a benzothiazole skeleton such as dihydrothio-p-toluidine and the like, a compound having a quinazoline skeleton such as quinazolidinedione and the like can be also used. Furthermore, a UV absorbent polymer can be used which is obtained by copolymerization of a radical polymerizable compound such as (meth)acrylic acid ester, styrene and the like with a radically polymerizable UV absorbent having a benzophenone skeleton or a benzotriazole skeleton. An inorganic compound such as titanium oxide, cerium oxide, zinc oxide, magnesium oxide and alumina can be also used. A pigment such as toluidine red, toluidine yellow, copper phthalocyanine, quinacridone, toluidine YW, Watchung red BWC, toluidine yellow GW, monastral blue BW, monastral green BW, pigment scarlet, monastral green, monastral maroon B, monastral orange, carbon black, graphite and the like can be used. Any one of these may be used or two or more kinds thereof may be concurrently used.

[0031] The proportion of the amounts of the aforementioned UV absorbing substances is 0.1 - 50 wt%, preferably 0.5 - 40 wt%, particularly desirably 1 - 30 wt%, relative to the organic polymer layer. When it is less than 0.1 wt%, UV absorbency dramatically decreases unpreferably showing no effect of enlarging exposure latitude. In contrast, when it exceeds 50 wt%, the time necessary for exposure to light becomes too long, thus impairing its practical applicability, and the organic polymer layer unpreferably becomes brittle.

[0032] The optical density of the UV absorbent organic polymer layer at 365 nm is preferably 0.05 - 1.00. When it is less than 0.05, it is ineffective for enlarging exposure latitude, and when it is 1.00 or above, the time necessary for exposure to light becomes too long, thus impairing its practical applicability.

[0033] As mentioned below, when the photosensitive resin laminate of the present invention is a photosensitive flexo plate, in one embodiment of the present invention, the above-mentioned organic polymer layer laminated on the metal layer is a non-IR-sensitive polymer resin layer, and the non-IR-sensitive polymer resin layer contains a water-soluble polymer and a plasticizer. The above-mentioned water-soluble polymer may be a copolymer with a substance having plasticity (plasticizer).

[0034] Examples of the water-soluble polymer are those recited above. As the plasticizer, any plasticizer generally usable for water-soluble polymer resins can be used. Examples of such plasticizer include alkylene glycols such as ethylene glycol, trimethylene glycol, tetramethylene glycol, propylene glycol, pentamethylene glycol, hexylene glycol, hexamethylene glycol and the like, polyalkylene glycols such as diethylene glycol, dipropylene glycol, triethylene glycol, tetraethylene glycol, polyethylene glycol #200, polyethylene glycol #300, polyethylene glycol #400, polyethylene glycol #600, polyethylene glycol #1000, polyethylene glycol #2000, polyethylene glycol #4000, a copolymer of polyethylene glycol and polypropylene glycol, and the like, butanediols such as 2,3-butanediol, 1,3-butanediol and the like, polyhydric alcohols such as alcohols of trivalent or more (e.g., glycerine, sorbitol, pentaerythritol, trimethylolpropane etc.) and the like, ethanolamines such as monoethanolamine, diethanolamine, triethanolamine and the like; amine compounds such as N-methylpyrrolidone, cyclohexylamine, urea and the like. Of these, polyethylene glycol, a copolymer of polyethylene

5 pylene glycol mono(meth)acrylate, polyethylene glycol monomethylether mono(meth)acrylate, polypropylene glycol monomethylether mono(meth)acrylate, polyethylene glycol monoethylether mono(meth)acrylate, polypropylene glycol monoethylether mono(meth)acrylate, n-butoxyethyl(meth)acrylate, phenoxyethyl(meth)acrylate, 2-phenoxypropyl (meth)acrylate, cyclohexyl(meth)acrylate, tetrahydrofuryl(meth)acrylate, glycidyl(meth)acrylate, allyl(meth)acrylate, benzyl(meth)acrylate, tribromophenyl(meth)acrylate, 2,3-dichloropropyl(meth)acrylate, 3-chloro-2-hydroxypropyl (meth)acrylate, N,N-diethylaminoethyl(meth)acrylate, N,N-dimethylaminoethyl(meth)acrylate, N-t-butylaminoethyl (meth)acrylate, acrylamide, N,N-dimethylacrylamide, N,N-diethylacrylamide, ethylene glycol di(meth)acrylate, diethylene glycol di(meth)acrylate, polyethylene glycol di(meth)acrylate, propylene glycol di(meth)acrylate, dipropylene glycol di(meth)acrylate, polypropylene glycol di(meth)acrylate, 1,3-butanediol (meth)acrylate, 1,4-butanediol (meth)acrylate, neopentylglycol di(meth)acrylate, 1,6-hexanediol di(meth)acrylate, 1,9-nonanediol di(meth)acrylate, 1,10-decanediol di(meth)acrylate, 1,12-dodecanediol di(meth)acrylate, 1,14-tetradecanediol di(meth)acrylate, pentaerythritol di (meth)acrylate, pentaerythritol tri(meth)acrylate, pentaerythritol tetra(meth)acrylate, glycelol di(meth)acrylate, glycelol allyloxy di(meth)acrylate, trimethylethane di(meth)acrylate, trimethylethane tri(meth)acrylate, trimethylolpropane di (meth)acrylate, trimethylolpropane tri(meth)acrylate, dicyclopentylmethylene di(meth)acrylate, dicyclopentadecane di(meth)acrylate, tricyclodecanediylmethyl di(meth)acrylate, triallylcyanurate, triallylisocyanurate, triallyltrimellitate, diallylphthalate, divinylbenzene, polyurethane (meth)acrylate, polyester (meth)acrylate, oligobutadiene (meth)acrylate, oligoisoprene (meth)acrylate, oligopropylene (meth)acrylate and the like, which may be used alone or in combination of two or more kinds thereof.

20 [0040] Preferable examples of the photoinitiator include benzophenones, benzoins, acetophenones, benzyls, benzoin alkylethers, benzylalkylketals, anthraquinones, thioxanthones and the like, which are specifically benzophenone, chlorobenzophenone, benzoin, acetophenone, benzyl, benzoin methylether, benzoin ethylether, benzoin isopropyl ether, benzoin isobutylether, benzylidimethylketal, benzylidethylketal, benzylidisopropylketal, anthraquinone, 2-ethyl-anthraquinone, 2-methylanthraquinone, 2-allylanthraquinone, 2-chloroanthraquinone, thioxanthone, 2-chlorothioxanthone and the like, which may be used alone or in combination of two or more kinds thereof.

25 [0041] The photosensitive resin layer in the present invention may contain, besides the polymer, the polymerizable compound and the photoinitiator, an additive such as a plasticizer, a thermal polymerization inhibitor, a dye, an antioxidant and the like.

30 [0042] The photosensitive resin layer can be prepared into a layer soluble or dispersible in a water-soluble developer, a semewater-soluble developer and an organic solvent developer by appropriately changing the materials of each component. It is preferably made to be developable in water or an aqueous medium. When preparing a photosensitive resin layer that can be developed in water or an aqueous medium, it preferably corresponds to the photosensitive resin layer specifically described in EP-A767407, JP-A-60-211451, JP-A-2-175702, JP-A-4-3162, JP-A-2-305805, JP-A-3-228060, JP-A-10-339951 and the like.

35 [0043] As mentioned below, when the photosensitive resin laminate of the present invention is a photosensitive letter press plate, in one embodiment of the present invention, the photosensitive resin layer has a residual solvent content of 3 - 10%, preferably 4 - 7%. When the residual solvent content is less than 3%, flowability during forming is degraded, which prevents delivery from a concentration machine or forming in a desired thickness. When the residual solvent content exceeds 10%, exposure of a photosensitive plate to actinic radiation without depressurization unpreferably causes inward curling during light exposure, which prevents uniform irradiation.

40 [0044] The residual solvent of a photosensitive resin layer in the present invention mainly consists of water and lower aliphatic alcohol, whose content is measured by the method to be mentioned below.

45 [0045] Examples of the aforementioned lower aliphatic alcohol include methyl alcohol, ethyl alcohol, propyl alcohol, isopropyl alcohol, ethylene glycol, ethylene glycol monomethylether and the like, and mixtures thereof. In view of handling property during production and the like, methyl alcohol and ethyl alcohol are preferably used.

50 [0046] When the photosensitive resin laminate of the present invention is a photosensitive letter press plate, the residual solvent component of the photosensitive resin layer of the present invention, the ratio of lower aliphatic alcohol and water is preferably 2/8 - 8/2, desirably 3/7 - 7/3. When the proportion of water exceeds 80%, concentration requires time and productivity is degraded. When it is less than 20%, a soluble synthetic polymer compound tends to show poor dissolution property and the dissolution time unpreferably becomes longer.

55 [0047] The support in the present invention is preferably a material having flexibility and superior in dimensional stability, and examples thereof include a film of metal such as steel, aluminum, copper, nickel and the like, a plastic film such as polyethylene terephthalate, polyethylene naphthalate, polybutylene terephthalate, polycarbonate and the like. Of these, polyethylene terephthalate film is used as a support material superior in dimensional stability and flexibility. The support used here desirably has a thickness of 50 - 350  $\mu\text{m}$ , preferably 100 - 250  $\mu\text{m}$ , in view of mechanical property, shape stability and handling property during printing plate making and the like. When the thickness is not more than 50  $\mu\text{m}$ , the support itself is subject to deformation such as bending and the like, and a thickness of not less than 350  $\mu\text{m}$  degrades flexibility to unpreferably cause lower fitting property to a cylinder during IR ablation. Where necessary, a generally used adhesive may be formed to improve adhesion between a support and a photosensitive

[0060] In the "rate of warp" in the present invention, a concave or convex change in the direction parallel to a side is referred to as a warp and expressed in a percentage of the maximum warp relative to the length of 100 mm. The concave is expressed in minus and the convex is expressed in plus. The change in the rate of warp means an absolute value of difference in the rate of warp before and after exposure to actinic radiation.

[0061] For the measurement of the rate of warp in the present invention, a photosensitive resin laminate having a diameter of 100 mm is measured for the rate of warp before exposure to actinic radiation after removing a protective film and the like, if such is on the IR ablation layer, to completely expose the IR ablation layer. Thereafter, 650 mJ actinic radiation is shot to the entire surface and the rate of warp is measured. The difference before and after the irradiation is calculated.

[0062] In the present invention, when the rate of warp exceeds  $\pm 2\%$  and when a photosensitive plate is placed on a light exposure machine without a decompression sheet, uniform irradiation at the time point when the plate is exposed to actinic radiation is not attainable. When changes in the rate of warp before and after the exposure to actinic radiation exceeds 15%, the photosensitive plate warps greatly during exposure to actinic radiation, which in turn causes inconsistent irradiation onto the plate and expression of lower resolution.

[0063] The method for preparing a photosensitive resin laminate of the present invention is not particularly limited but generally, a photosensitive resin layer is formed on a support by applying, spray coating and the like to give one of the two laminates, or a protective film is peeled off from a commercially available photosensitive printing plate to give one laminate. Separately, an organic polymer layer is formed by applying, spray coating and the like on a substrate film (cover film), then forming an IR absorbent metal layer by vacuum deposition, sputtering and the like to give the other laminate. The thus-obtained two laminates are laminated using a heat press machinery and the like. The laminating conditions are temperature: room temperature to 150°C, preferably 50 - 120°C, pressure: 20 - 200 kg-weight/cm<sup>2</sup>, preferably 50 - 150 kg-weight/cm<sup>2</sup>.

[0064] The use of the photosensitive resin laminate of the present invention is not particularly limited and is exemplified by plate for printing, sign plate, plate for forming mother die, mask material for flexible printed circuit and the like. The plate for printing includes, for example, flexo plate, letter press plate, plate for pad printing (plate for intaglio printing), plate for screen printing, plate for lithographic printing and the like. In one embodiment of the present invention, the above-mentioned photosensitive resin laminate is a photosensitive plate.

[0065] In one embodiment of the present invention, the above-mentioned photosensitive resin laminate is a photosensitive flexo plate or photosensitive letter press plate.

[0066] The photosensitive resin laminate of the present invention has at least a support, a photosensitive resin layer and an IR ablation layer, wherein the IR ablation layer contains an IR absorbent metal layer and the metal layer has a UV absorbent organic polymer layer on at least one surface.

[0067] Preferable embodiments of the above-mentioned support, photosensitive resin layer, IR ablation layer, IR absorbent metal layer and UV absorbent organic polymer layer are as described in the above.

[0068] A printing plate or a relief plate can be prepared from a photosensitive plate as in the following.

[0069] After a cover film is or is not peeled off, an ablation layer is exposed to IR laser image for IR ablation, whereby a mask is formed on a photosensitive resin layer. Examples of suitable IR laser include ND/YAG laser (1064 nm) and diode laser (e.g., 830 nm). A laser system suitable for a computer plate making technique is commercially available, and exemplified by Cyrel Digital Imager Spark (manufactured by BARCO), diode laser system OmniSetter (registered trademark) (laser wavelength: 830 nm; drum axis: 1800 mm) and ND/YAG laser system Digilas (registered trademark). These include a rotary cylindrical drum to support a photosensitive plate, an IR laser irradiation apparatus and a layout computer. The image information is directly transmitted from the layout computer to the laser apparatus.

[0070] After writing the mask on the IR ablation layer as mentioned above, the photosensitive plate is entirely exposed to actinic radiation through the mask. This is advantageously done directly on the laser cylinder. Alternatively, the plate may be removed from the laser apparatus and exposed to actinic radiation on a conventional flat irradiation unit. During the irradiation step, the photosensitive resin layer polymerizes in the area exposed in the above-mentioned mask forming step (ablation step) and otherwise in the IR ablation layer area which is covered with the IR ablation layer non-transparent to irradiation light. The actinic radiation may be applied in a conventional vacuum frame without oxygen. It may be also applied in the presence of atmospheric oxygen.

[0071] When an image written by IR laser needs modification before the above-mentioned exposure of the entire surface to actinic radiation in the present invention, an opaque is applied onto the polymer resin layer to enable easy modification of the image. In one embodiment of the present invention, an organic polymer layer laminated on the metal layer can receive an opaque non-transparent to the actinic radiation. The opaque in the present invention is a substance that substantially prevents transmission of ultraviolet rays (actinic radiation). Examples thereof include oil-based ink, water-based ink, light blocking opaque tape and the like. Preferred is one having an optical density of not less than 2.0 for actinic radiation.

[0072] After exposure to actinic radiation as mentioned above, the plate is subjected to development. The development step can be performed using a conventional development unit, and depending on the properties of the plate,

## (Reference Example 4)

[0079] An aqueous solution of polyvinyl alcohol (GOHSENOL GH-23 manufactured by NIPPON SYNTHETIC CHEMICAL INDUSTRY CO., LTD., degree of saponification: 88%)/copolymer of polyethylene glycol and polypropylene glycol (SANFLEX SE270 manufactured by Sanyo Chemical Industries, Ltd.)/surfactant (EPAN 740 manufactured by Dai-ichi Kogyo Seiyaku Co., Ltd.)/pure water=10.0 g/7.5 g/0.01 g/332.5 g was applied to a PET film (whole cloth was manufactured by Toyo Boseki Kabushiki Kaisha, E5002, thickness 125 µm, chemical matte treatment performed by TOYOCLOTH CO., LTD.), that had undergone a chemical matte treatment with a barcoater #26, and dried at 100°C for 3 min to form a film having a thickness after drying of 1.8 µm. Then, aluminum was evaporated on the surface of the film by vacuum deposition process in a thickness of about 500 Å. The optical density at this time was 3.0.

## (Reference Example 5)

[0080] An aqueous solution of polyvinyl alcohol (GOHSENOL KH20 manufactured by NIPPON SYNTHETIC CHEMICAL INDUSTRY CO., LTD., degree of saponification: 80%)/polyethylene glycol #600 (manufactured by Nacalai Tesque, Inc.)/UV absorbent WF-825 (manufactured by SANNAN KAGAKU)/pure water=2.0 g/1.0 g/0.5 g/106.5 g was applied to a PET film (E5002, whole cloth was manufactured by Toyo Boseki Kabushiki Kaisha, thickness 125 µm, chemical matte treatment performed by TOYOCLOTH CO., LTD.), that had undergone a chemical matte treatment with a barcoater #26, and dried at 100°C for 3 min to form a film having a thickness after drying of 2 µm. Then, aluminum was evaporated on the surface of the film by vacuum deposition process in a thickness of about 800 Å. The optical density at this time was 4.5.

## (Comparison Reference Example 1)

[0081] Using the components shown in the following Table 1, a dispersion containing carbon black, polyvinyl alcohol (GOHSENOL GH-23, manufactured by NIPPON SYNTHETIC CHEMICAL INDUSTRY CO., LTD., degree of saponification: 88%) and a plasticizer was prepared. This dispersion was applied onto a PET film (thickness 125 µm) with a #26 barcoater and dried at 100°C for 3 min to evaporate water, whereby smooth non-adhesive coating film (coated amount 4.1 g/m<sup>2</sup> and optical density of actinic radiation area 4.8) was obtained, or a cover film having an IR ablation layer.

Table 1

Component	Amount added (g)	Weight without water (g)	Note
3% aqueous solution of GH-23	53.9	36.3	
polyethylene glycol #400	1.13	25.4	plasticizer
EPAN 740	0.004	0.09	dispersant (surfactant)
carbon black CW1	8.5	38.2	20% aqueous dispersion
distilled water	36.0	-	

Carbon black CW1: manufactured by Orient Chemical Industries, Ltd.

## (Example 1)

[0082] A chemical matte PET protective film was released from a photosensitive flexo printing plate (Cosmolight NEO, manufactured by Toyo Boseki Kabushiki Kaisha) consisting of a 100 µm thick PET film support (E5002, manufactured by Toyo Boseki Kabushiki Kaisha), a photosensitive resin layer, a polyvinyl alcohol layer and a chemical matte PET protective film, and a polyvinyl alcohol layer thereunder was removed from the photosensitive resin layer using a conventional adhesive tape. The deposit surface of the aluminum deposited film prepared in Reference Example 1 was superimposed on the exposed photosensitive resin layer, and laminated using a heat press machine at 100°C, 100 kg-weight/cm<sup>2</sup> to give a plate consisting of a PET support, a photosensitive resin layer, an aluminum deposit layer, a polyvinyl alcohol layer and a chemical matte PET protective film (cover film). The total thickness of this plate was 1.90 mm.

[0083] For back exposure to make the relief depth a generally employed depth of about 0.8 mm, the PET support side of the above-mentioned flexo plate was exposed to actinic radiation (light source: Philips 10R, illuminance at 365 nm 7.5 mW/cm<sup>2</sup>) for 20 sec, and the chemical matte PET protective film (cover film) was peeled off. At this time, the

for 2 min with a developing machine (JEM-A2, manufactured by NIHON DENSHI SEIKI CO., LTD.). As a developer, used was tap water. During development, the remaining IR ablation layer (aluminum deposited layer, polyvinyl alcohol layer) and non-irradiation areas of the photosensitive resin layer were removed, leaving the area exposed to actinic radiation. After the development, the plate was dried at 70°C for 10 min and exposed to actinic radiation for 3 min.

[0091] The finished resin relief printing plate was examined with a loupe (10× magnification). Fogging was not observed and all the test patterns of 2 point convex part and concave letters, 30 µm wide fine line, 100 µm diameter isolated dot and 156 lpi, 1% halftone dot were found to have been correctly formed.

(Example 4)

[0092] A nylon salt (390 parts by weight) of ε-caprolactam (610 parts by weight), aminoethylpiperazine and adipic acid was melt polymerized to give a copolymerized polyamide. The thus-obtained polyamide (50 parts) was dissolved in methanol (200 parts) and water (24 parts), and itaconic acid (4 parts), adipic acid (4 parts), bisphenol A diglycidyl ether acrylic acid adduct (32 parts), N-ethyl-p-toluenesulfonamide (8 parts), hydroquinone monomethylether (0.1 part) and benzylidemethylketal (1 part) were added to this solution to give a photosensitive resin composition solution. This solution was delivered to a concentrating machine and concentrated at 110°C to achieve a residual solvent content of the photosensitive resin layer of 5% and a methanol:water ratio of 6:4, which was sandwiched between a 250 µ thick PET film coated with a 20 µ thick adhesive and a film having the IR ablation layer of Reference Example 1 and melt formed at 110°C to give a photosensitive flexo plate having a 680 µ thick photosensitive resin layer. The warp of this plate was measured and found to be 0% before exposure to actinic radiation and 10% of change in warp after exposure to actinic radiation. The cover film was removed from this plate and the IR ablation layer after recording an image was exposed to actinic radiation for 3 min without depressurization. The plate was developed with neutral water at 25°C for 2 min and dried at 70°C for 10 min. The obtained photosensitive resin showed a sensitivity of 14 steps and the resin hardness by Shore D was 57. The image reproducibility of the printed matter was satisfactory.

(Example 5)

[0093] In the same manner as in Example 1 except that the aluminum deposited layer obtained in Reference Example 2 was used, a flexo printing plate was obtained. The obtained flexo printing plate was examined with a loupe (10× magnification). Fogging phenomenon was not observed and all the test patterns of 2 point convex part and concave letters, 30 µm wide fine line, 100 µm diameter isolated dot and 156 lpi, 1% halftone dot were found to have been correctly formed.

(Example 6)

[0094] In the same manner as in Example 3 except that the aluminum deposited layer obtained in Reference Example 2 was used, a photosensitive resin relief plate was obtained. The obtained relief plate was examined with a loupe (10× magnification). Fogging was not observed and all the test patterns of 2 point convex part and concave letters, 30 µm wide fine line, 100 µm diameter isolated dot and 156 lpi, 1% halftone dot were found to have been correctly formed.

(Example 7)

[0095] In the same manner as in Example 1 except that the aluminum foil layer obtained in Reference Example 3 was used, a flexo printing plate was obtained. The obtained flexo printing plate was examined with a loupe (10× magnification). Fogging was not observed and all the test patterns of 2 point convex part and concave letters, 30 µm wide fine line, 100 µm diameter isolated dot and 156 lpi, 1% halftone dot were found to have been correctly formed.

(Example 8)

[0096] In the same manner as in Example 3 except that the aluminum foil layer obtained in Reference Example 3 was used, a photosensitive resin relief plate was obtained. The obtained relief plate was examined with a loupe (10× magnification). Fogging was not observed and all the test patterns of 2 point convex part and concave letters, 30 µm wide fine line, 100 µm diameter isolated dot and 156 lpi, 1% halftone dot were found to have been correctly formed.

(Example 9)

[0097] In the same manner as in Example 1 except that the aluminum deposited layer obtained in Reference Example 4 was used, a flexo plate was obtained. A chemical matte PET cover film of the obtained plate was peeled off, wound

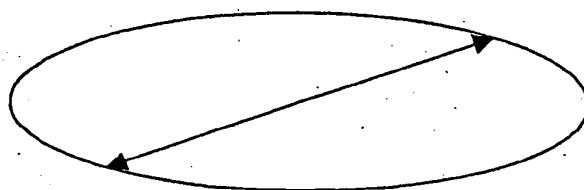
which in turn affords a printing plate that provides high quality printing images. In addition, due to less stain of the developer during development, successive development of plural plates is attainable. Therefore, the present invention contributes greatly to the industry.

5

### Claims

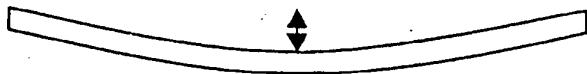
1. A photosensitive resin laminate comprising at least a support, a photosensitive resin layer and an IR ablation layer, wherein the IR ablation layer comprises an IR absorbent metal layer which is disposed in contact with the photosensitive resin layer.
2. The photosensitive resin laminate of claim 1, wherein the IR ablation layer comprises the IR absorbent metal layer and an organic polymer layer laminated on said metal layer.
3. The photosensitive resin laminate of claim 1, wherein the IR ablation layer has a thickness of 70 - 20000 Å.
4. The photosensitive resin laminate of claim 1, wherein the IR absorbent metal layer is an aluminized layer.
5. The photosensitive resin laminate of claim 2, wherein the organic polymer layer laminated on the metal layer is a non-IR-sensitive polymer resin layer.
6. The photosensitive resin laminate of claim 2, wherein the organic polymer layer laminated on the metal layer can receive an opaque non-transparent to actinic radiation.
7. The photosensitive resin laminate of claim 2, wherein the organic polymer layer laminated on the metal layer contains a UV absorbent.
8. The photosensitive resin laminate of claim 1, wherein the IR ablation layer has an optical density of not less than 2.0.
9. The photosensitive resin laminate of claim 1, which shows a rate of change in the radius of a halftone dot after IR ablation of not more than  $\pm 30\%$  per unit energy ( $J/cm^2$ ).
10. The photosensitive resin laminate of claim 1, which is a photosensitive plate.
11. The photosensitive resin laminate of claim 1, which is a photosensitive flexo plate.
12. The photosensitive resin laminate of claim 11, wherein wrinkles are not caused when a bending radius is not more than 5 cm.
13. The photosensitive resin laminate of claim 11, wherein the IR ablation layer comprises the IR absorbent metal layer and an organic polymer layer laminated on said metal layer, said organic polymer layer being a non-IR-sensitive polymer resin layer and the non-IR-sensitive polymer resin layer comprising a water-soluble polymer and a plasticizer.
14. The photosensitive resin laminate of claim 1, wherein the photosensitive resin laminate is a photosensitive letter press plate.
15. The photosensitive resin laminate of claim 14, wherein the photosensitive resin layer comprises a composition comprising a polymer binder, an ethylenically unsaturated compound and a photoinitiator, the photosensitive resin laminate shows a rate of warp of within  $\pm 2\%$  before exposure to actinic radiation, and a change in the warp after exposure to actinic radiation is not more than 15%.
16. The photosensitive resin laminate of claim 14, wherein the photosensitive resin layer has a residual solvent content of 3 - 10%.
17. A photosensitive resin laminate comprising at least a support, a photosensitive resin layer and an IR ablation layer, wherein the IR ablation layer comprises an IR absorbent metal layer and a UV absorbent organic polymer layer on at least one surface of the metal layer.

**FIG. 4**



diameter 100 mm

**FIG. 5**



maximum warp

ANNEX TO THE EUROPEAN SEARCH REPORT  
ON EUROPEAN PATENT APPLICATION NO.

EP 02 02 3876

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

12-02-2003

Patent document cited in search report		Publication date		Patent family member(s)	Publication date
EP 1146392	A	17-10-2001	EP	1146392 A1	17-10-2001
			JP	2001356491 A	26-12-2001
			US	2001038975 A1	08-11-2001
US 6245486	B1	12-06-2001		NONE	
US 4132168	A	02-01-1979	CA	1049312 A1	27-02-1979
			DE	2500907 A1	24-07-1975
			FR	2258649 A1	18-08-1975
			GB	1492070 A	16-11-1977
			IT	1026287 B	20-09-1978
			JP	50102401 A	13-08-1975
			JP	51006568 B	28-02-1976
WO 0163364	A	30-08-2001	US	6367381 B1	09-04-2002
			AU	1770401 A	03-09-2001
			EP	1257881 A1	20-11-2002
			WO	0163364 A1	30-08-2001